ONR Topic Chief: David Shifler

Tailoring of Atomic-Scale Interphase Complexions for Mechanism-Informed Material Design

ONR Grant N00014-11-1-0678

Martin P. Harmer

Start: June 1, 2011
End: May 31, 2016

Budget: $1.5M per year

MURI Team Members

Martin P. Harmer

LEHIGH UNIVERSITY

Gregory S. Rohrer

Carnegie Mellon University

Jian Luo

UC San Diego

Helen M. Chan

LEHIGH UNIVERSITY

Anthony D. Rollett

Carnegie Mellon University

Shen J. Dillon

ILLINOIS
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Jeffrey M. Rickman

LEHIGH UNIVERSITY

Michael Widom

Carnegie Mellon University

Andrea J. Harmer

KUTZTOWN UNIVERSITY

13 Graduate Students | **3 Postdoctoral Research Associates**

5 Females | **9 U.S. citizens**

Collaborators: Eduardo Saiz Gutierrez (Imperial College), Rick Vinci (Lehigh), Ed Webb (Lehigh)

Meetings & Conferences

Meetings

- Pre-Kick Off Meeting Web Conference, June 10, 2011
- Kickoff Meeting, Lehigh University, June 23, 2011
- Web Conference, October 31, 2011
- Pre-Review Planning Meeting, CMU, November 28, 2011
- **1st Review Meeting, Washington, DC, December 15, 2011**
- Sub-Group Meeting, February 12, 2012
- Pre-Review Planning Meeting, Lehigh University, May 17, 2012
- ONR Program Review, High Temperature and Cellular Materials, Charleston, SC, May 31, 2012
- **2nd Review Meeting, Lehigh University, June 8, 2012**
- Pre-Review Planning Meeting, CMU and Online, December 3, 2012
- **3rd Review Meeting, Washington, DC, December 18, 2012**
- Pre-Review Planning Meeting, Lehigh University, April 9, 2013
- ONR Program Review, High Temperature and Cellular Materials, Bozeman, MT, May 30, 2013
- **4th Review Meeting, San Diego, CA, June 7, 2013 (cancelled)**

Conferences

- MS&T, Columbus, OH, October 18, 2011
- TMS, Orlando, FL, March 11-15, 2012
- Gordon Conference, New Hampshire, August 2012
- **Bear Creek International Workshop on Interfaces, Macungie, PA, October 2-6, 2012**
- MS&T, Pittsburgh, PA, October 2012
- TMS, San Antonio, TX, March 2013

Journal Articles & Website

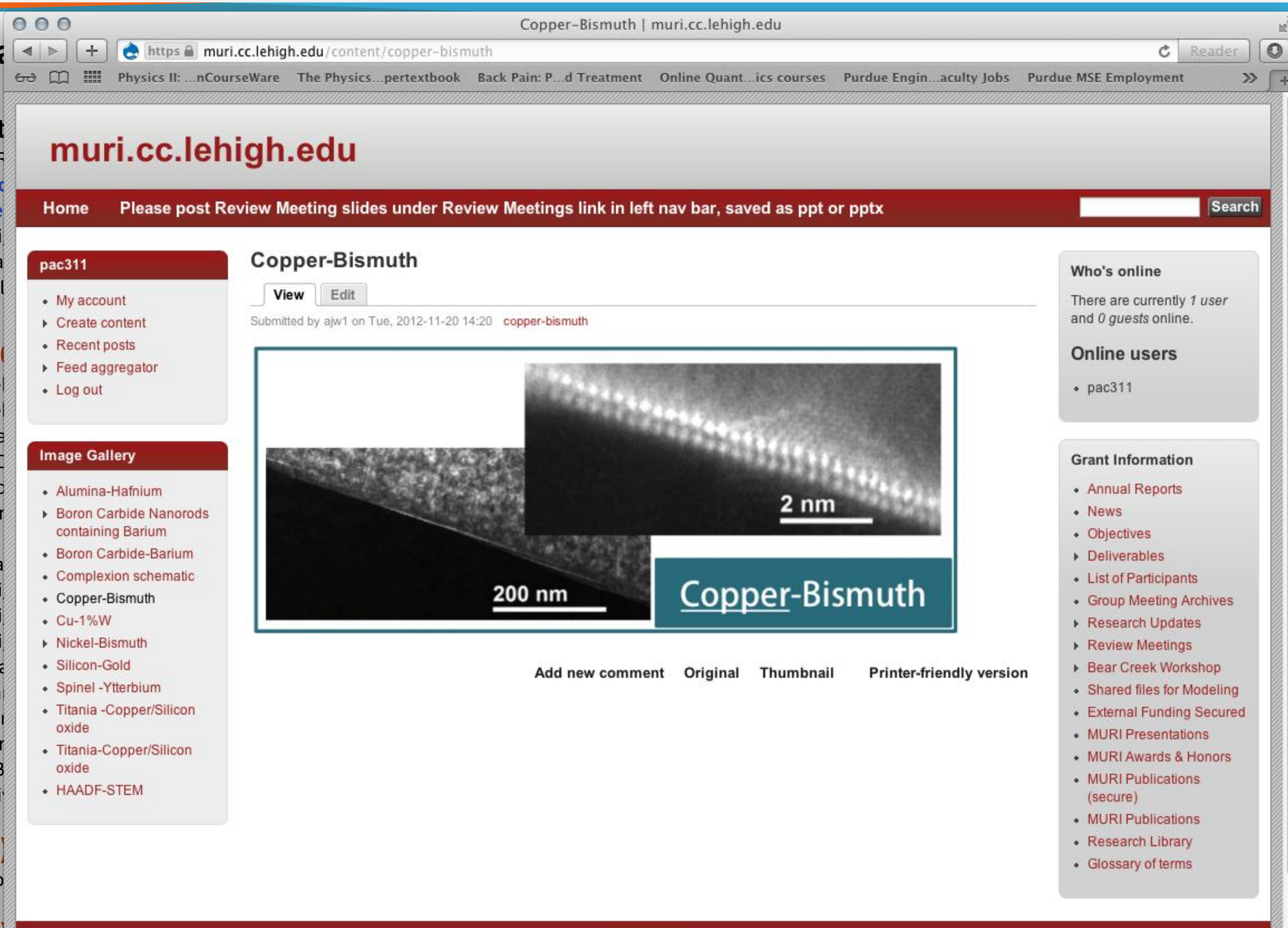
Journa

Submitt
- J.M. F
- Patric … Acta Mate
- K. Tai
- Q. Ga
- C.-Y. L

2013 (1
- H. Bel
- H. Bel
- W. Ca
- A.D. D … py and Micro
- S. Cur
- R. M. … 6(R).
- S. Ma
- K. Tai
- K. Tai
- K. Tai
- X. Yu
- Zhiya
- A. Ku
- S. Cur
- S.A. B
- N. Sri

2012 (1)
- J. Luo

2011 (1)
- J. Luo, H. Cheng, K. Meshinchi Asl, C..J. Kiely, and M. P. Harmer, *Science*, **333** (2011) 1730-1733.



Scientific Purpose & Background

Grain Boundaries

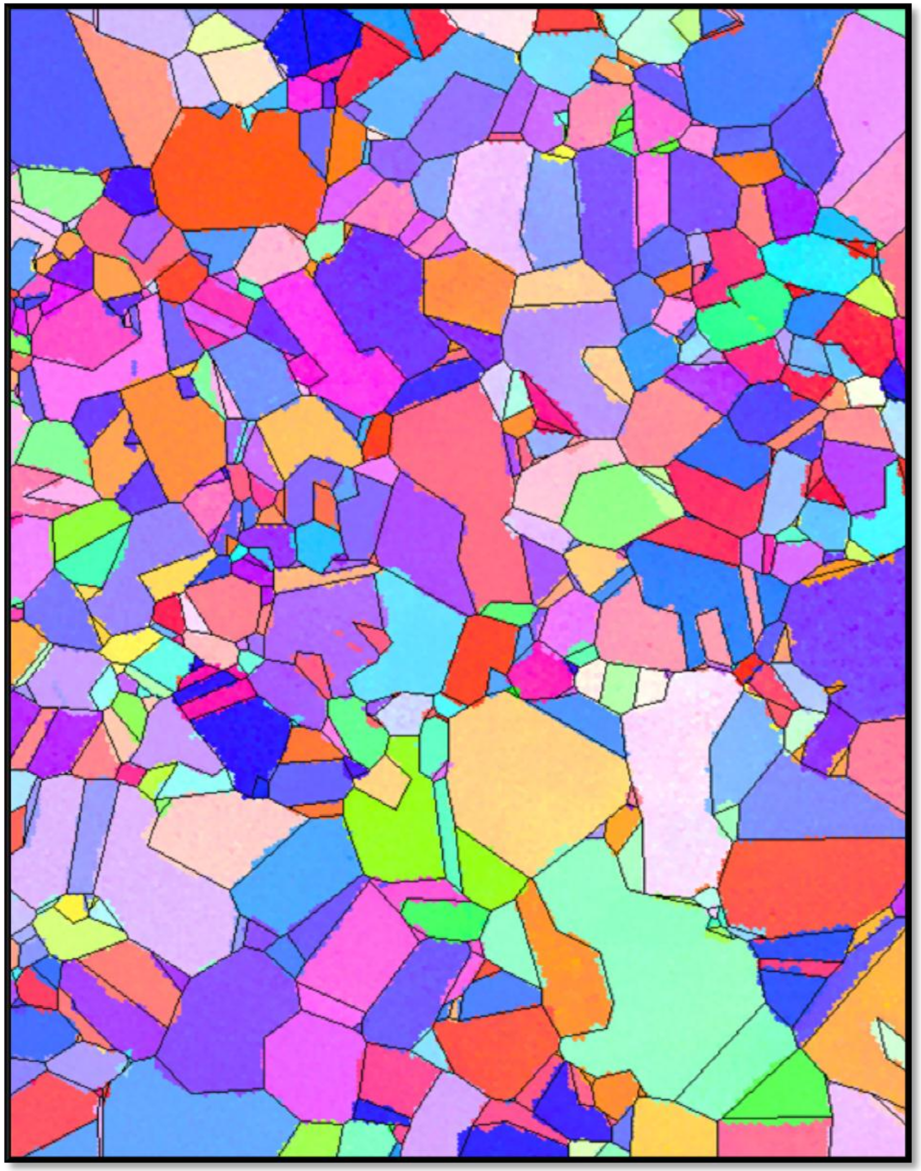
Fabrication and Processing
Cold-working, annealing, recrystallization…

Related Phenomena and Properties
Ductility, creep, oxidation…

…but how much do we really know?

How do we explain _discontinuities_ in grain boundary-related properties?

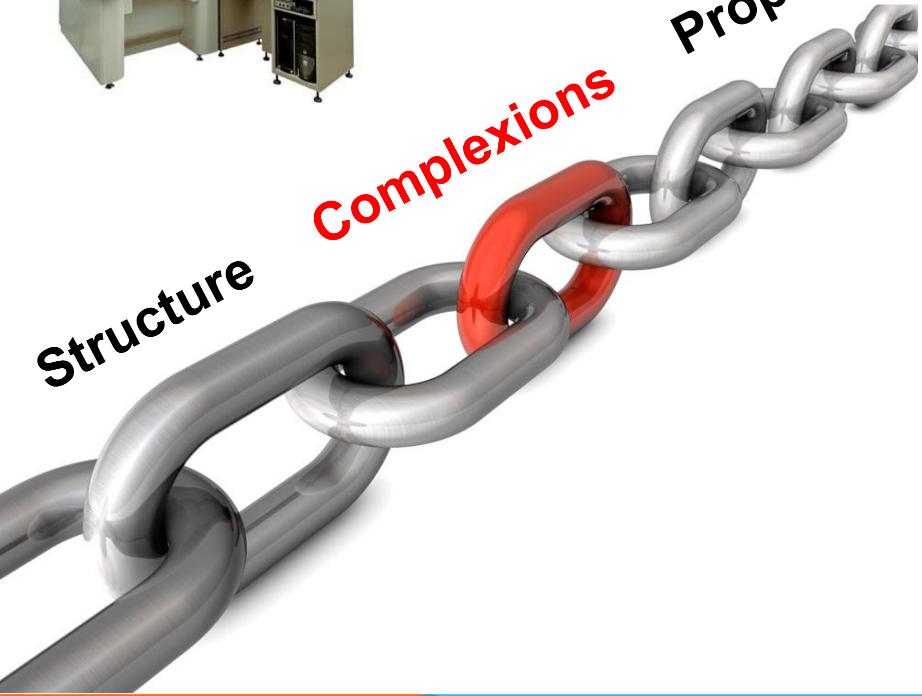
- Abnormal grain growth?
- Embrittlement?
- Nanocrystalline thermal (in)stability?

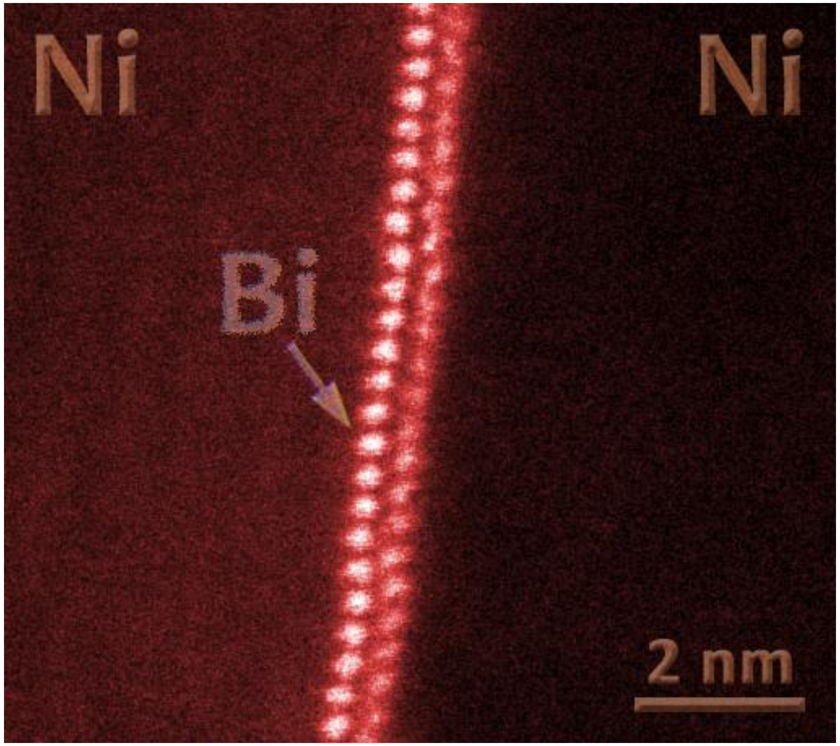


Scientific Background: Phase-like Behavior of GBs

Complexion
The interfacial analogue to a bulk phase

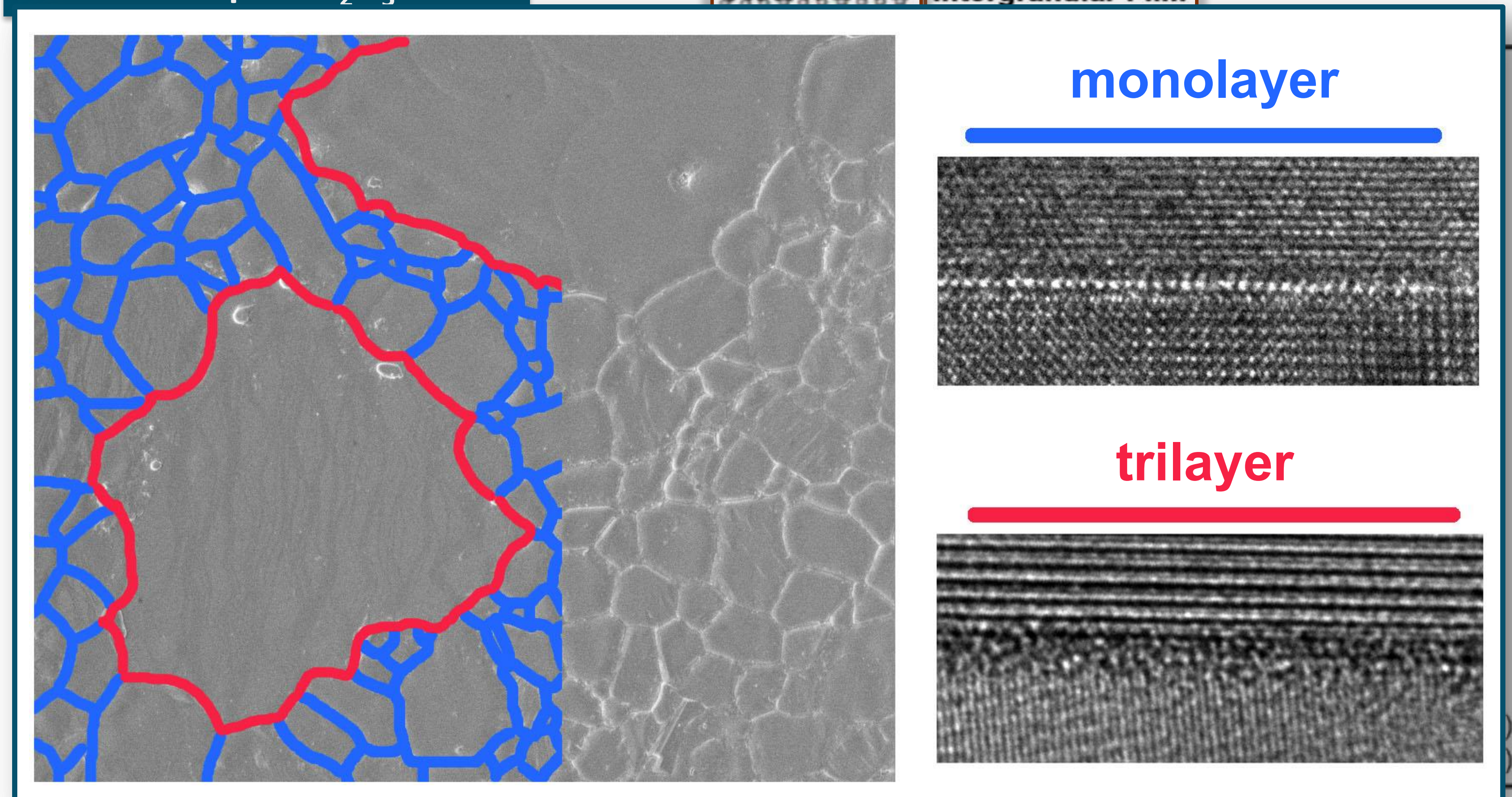
Aberration-Corrected
Scanning Transmission
Electron Microscopy

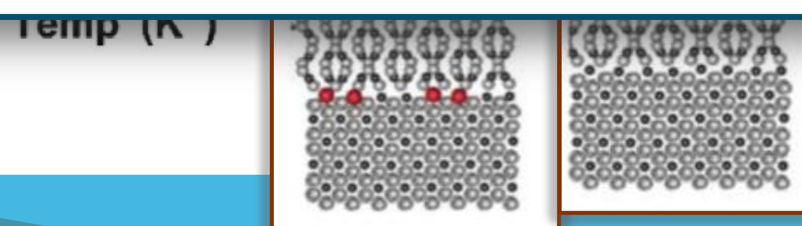




Scientific Background: Phase-like Behavior of GBs

Grain Boundary Mobility in Doped Al_2O_3





SJ Dillon, M Tang, WC Carter, MP Harmer, Acta Mater. **55** (2007) 6208

Goals of the Program & General Approach

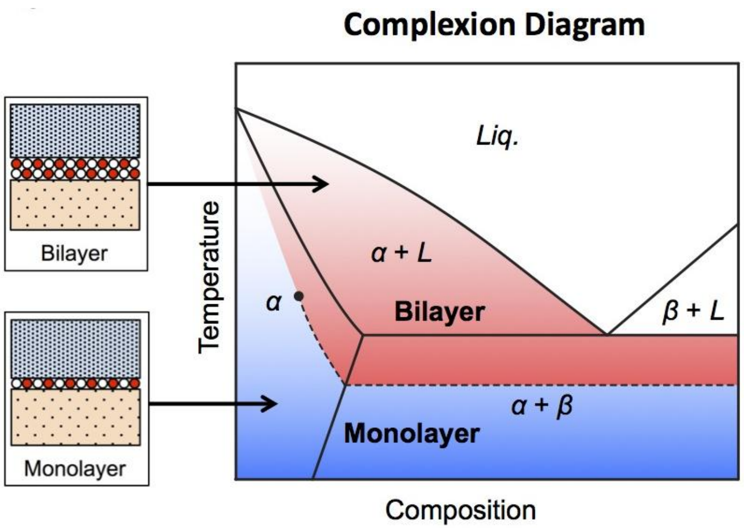
Grain Boundary Complexion Diagrams

Analogous to Bulk Phase Diagrams

- 5 additional thermodynamic degrees of freedom

Multi-disciplinary approach

- **Experiments**: grain growth, diffusion, conductivity thermal properties…
- **Simulation**: Density functional theory (DFT), molecular dynamics (MD)…
- **Theory:** Thermodynamic computational methods



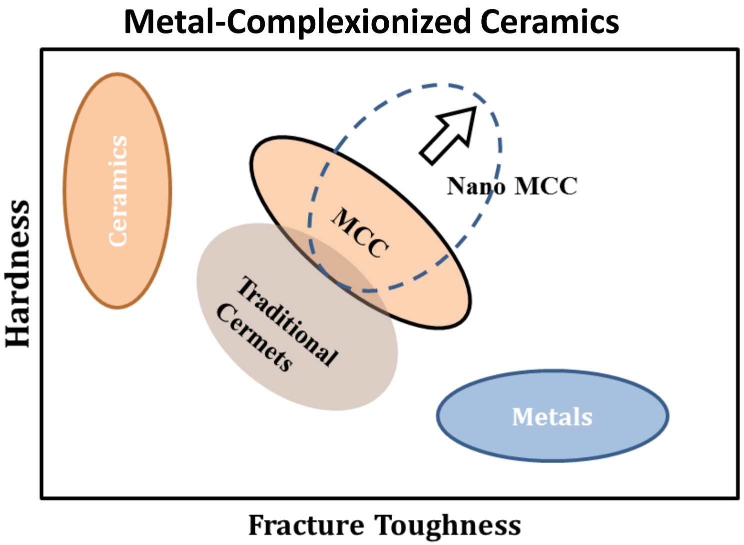
New & Improved Materials

Metal-Complexionized Ceramics

- Metallic complexions at ceramic grain boundaries

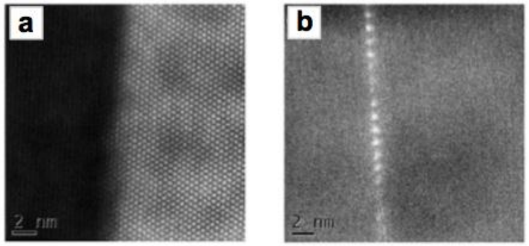
Thermally Stable Nanocrystalline Metals

- Understanding mechanism of thermal stability

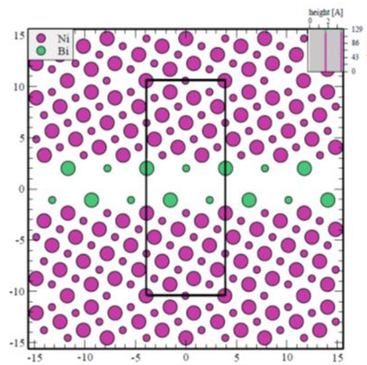


Plotting Complexion Diagrams

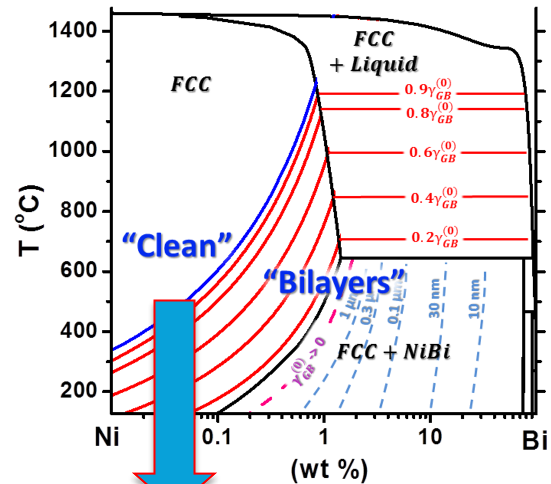
Electron Microscopy



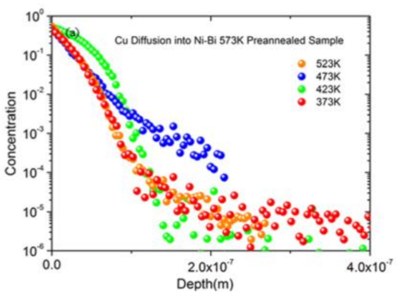
DFT Simulations



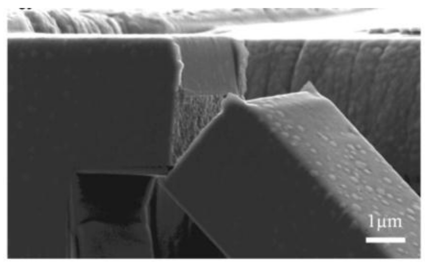
Thermodynamic Models



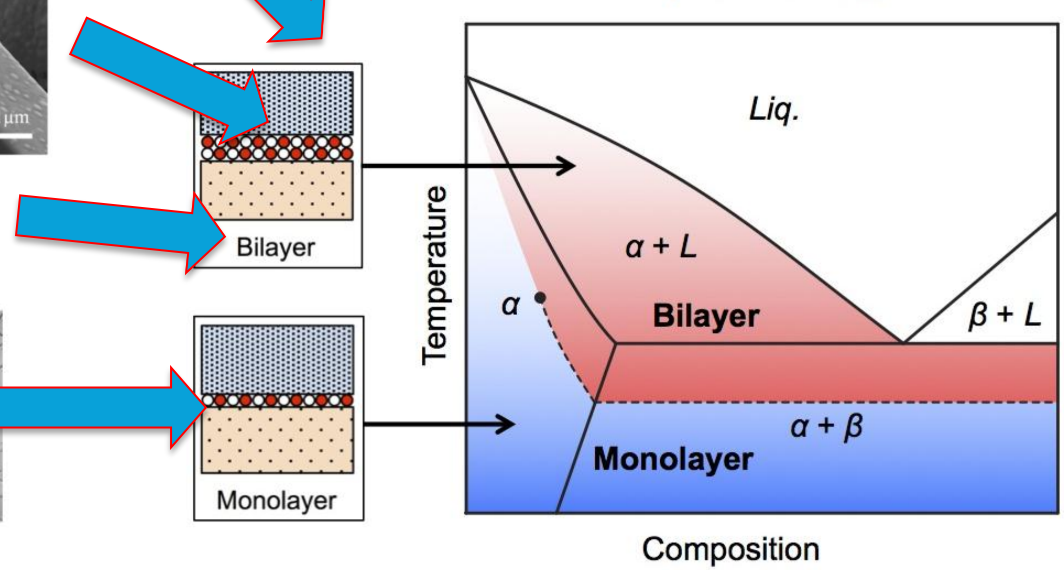
GB Diffusivity



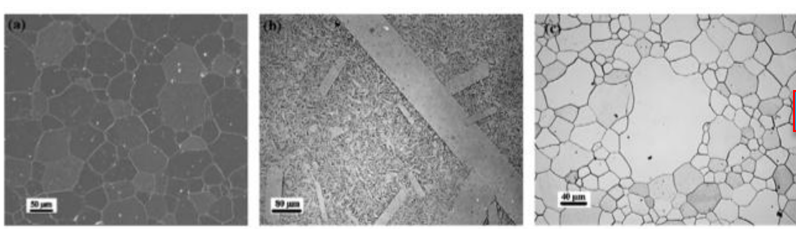
Mechanical Properties



Complexion Diagram

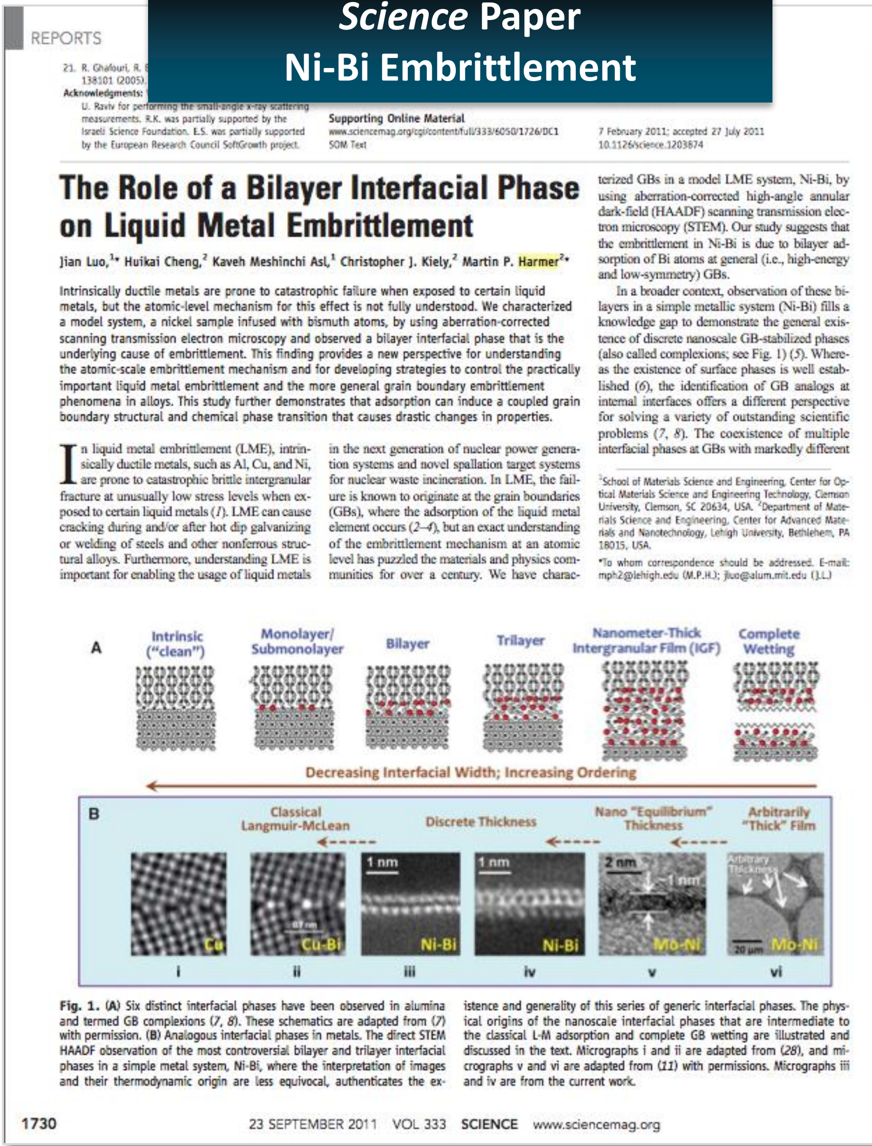


GB Mobility



Accomplishments: Liquid Metal Embrittlement

Science Paper
Ni-Bi Embrittlement



REPORTS

21. R. Ghafouri, R.
138101 (2005).

Acknowledgments:
U. Raviv for performing the small-angle x-ray scattering measurements. R.K. was partially supported by the Israeli Science Foundation. E.S. was partially supported by the European Research Council SoftGrowth project.

Supporting Online Material
www.sciencemag.org/cgi/content/full/333/6050/1726/DC1
SOM Text

7 February 2011; accepted 27 July 2011
10.1126/science.1203874

The Role of a Bilayer Interfacial Phase on Liquid Metal Embrittlement

Jian Luo,[1*] Huikai Cheng,[2] Kaveh Meshinchi Asl,[1] Christopher J. Kiely,[2] Martin P. Harmer[2*]

Intrinsically ductile metals are prone to catastrophic failure when exposed to certain liquid metals, but the atomic-level mechanism for this effect is not fully understood. We characterized a model system, a nickel sample infused with bismuth atoms, by using aberration-corrected scanning transmission electron microscopy and observed a bilayer interfacial phase that is the underlying cause of embrittlement. This finding provides a new perspective for understanding the atomic-scale embrittlement mechanism and for developing strategies to control the practically important liquid metal embrittlement and the more general grain boundary embrittlement phenomena in alloys. This study further demonstrates that adsorption can induce a coupled grain boundary structural and chemical phase transition that causes drastic changes in properties.

In liquid metal embrittlement (LME), intrinsically ductile metals, such as Al, Cu, and Ni, are prone to catastrophic brittle intergranular fracture at unusually low stress levels when exposed to certain liquid metals (*1*). LME can cause cracking during and/or after hot dip galvanizing or welding of steels and other nonferrous structural alloys. Furthermore, understanding LME is important for enabling the usage of liquid metals in the next generation of nuclear power generation systems and novel spallation target systems for nuclear waste incineration. In LME, the failure is known to originate at the grain boundaries (GBs), where the adsorption of the liquid metal element occurs (*2*–*4*), but an exact understanding of the embrittlement mechanism at an atomic level has puzzled the materials and physics communities for over a century. We have characterized GBs in a model LME system, Ni-Bi, by using aberration-corrected high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM). Our study suggests that the embrittlement in Ni-Bi is due to bilayer adsorption of Bi atoms at general (i.e., high-energy and low-symmetry) GBs.

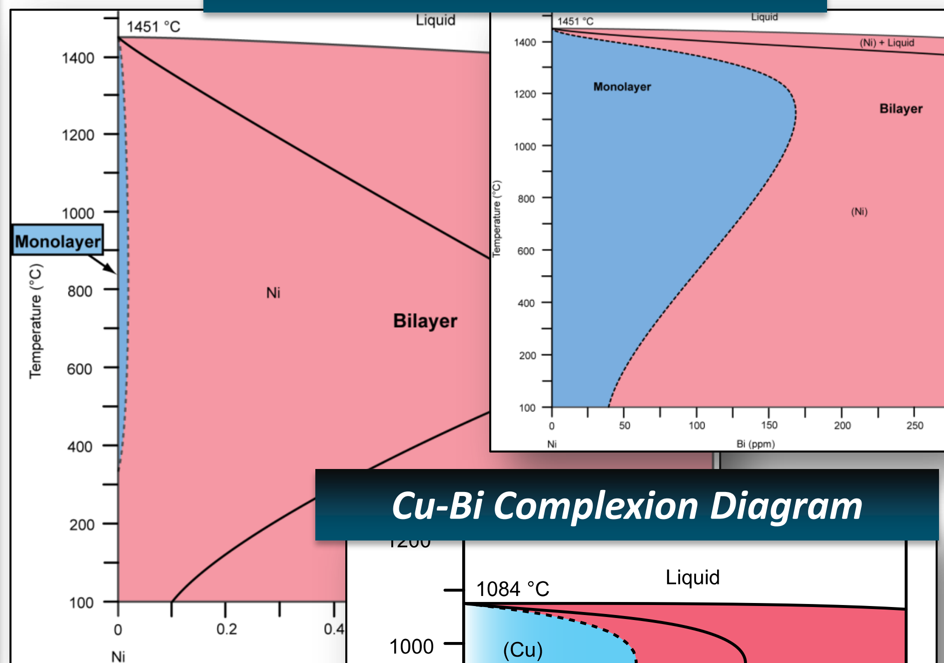
In a broader context, observation of these bilayers in a simple metallic system (Ni-Bi) fills a knowledge gap to demonstrate the general existence of discrete nanoscale GB-stabilized phases (also called complexions; see Fig. 1) (*5*). Whereas the existence of surface phases is well established (*6*), the identification of GB analogs at internal interfaces offers a different perspective for solving a variety of outstanding scientific problems (*7*, *8*). The coexistence of multiple interfacial phases at GBs with markedly different

[1]School of Materials Science and Engineering, Center for Optical Materials Science and Engineering Technology, Clemson University, Clemson, SC 20634, USA. [2]Department of Materials Science and Engineering, Center for Advanced Materials and Nanotechnology, Lehigh University, Bethlehem, PA 18015, USA.
*To whom correspondence should be addressed. E-mail: mph2@lehigh.edu (M.P.H.); jluo@alum.mit.edu (J.L.)

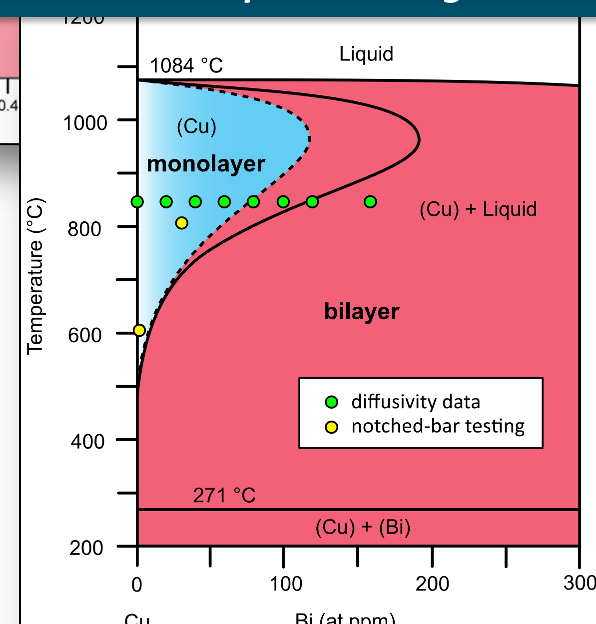
Fig. 1. (**A**) Six distinct interfacial phases have been observed in alumina and termed GB complexions (*7*, *8*). These schematics are adapted from (*7*) with permission. (**B**) Analogous interfacial phases in metals. The direct STEM HAADF observation of the most controversial bilayer and trilayer interfacial phases in a simple metal system, Ni-Bi, where the interpretation of images and their thermodynamic origin are less equivocal, authenticates the existence and generality of this series of generic interfacial phases. The physical origins of the nanoscale interfacial phases that are intermediate to the classical L-M adsorption and complete GB wetting are illustrated and discussed in the text. Micrographs i and ii are adapted from (*28*), and micrographs v and vi are adapted from (*11*) with permissions. Micrographs iii and iv are from the current work.

1730 23 SEPTEMBER 2011 VOL 333 SCIENCE www.sciencemag.org

Ni-Bi Complexion Diagram

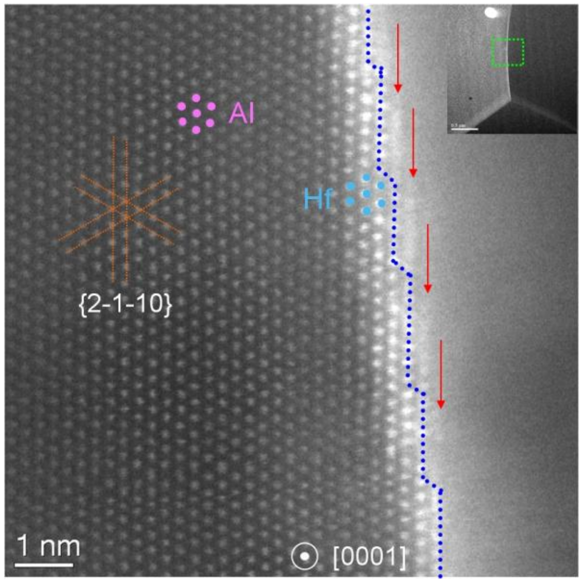


Cu-Bi Complexion Diagram



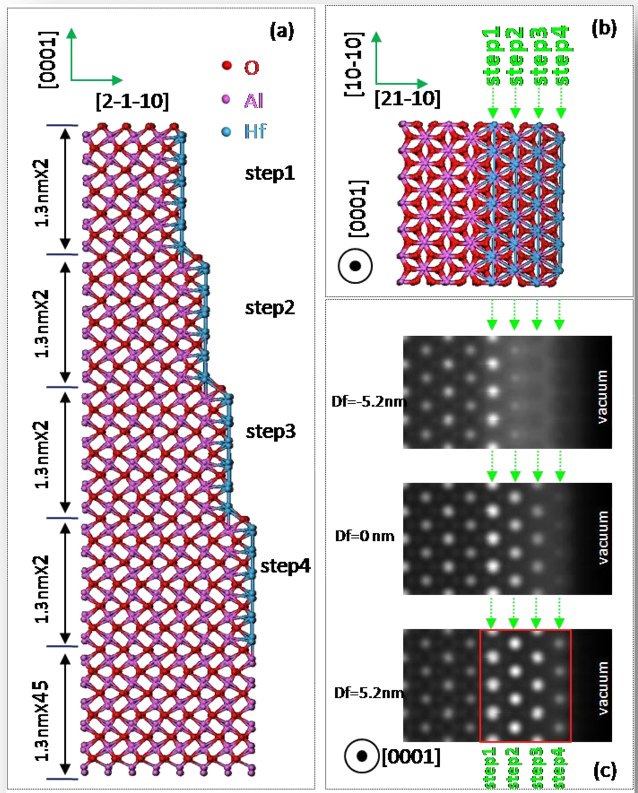
Accomplishments: Al_2O_3-HfO_2

Currently Under Investigation: Hf-doped Polycrystalline Al_2O_3

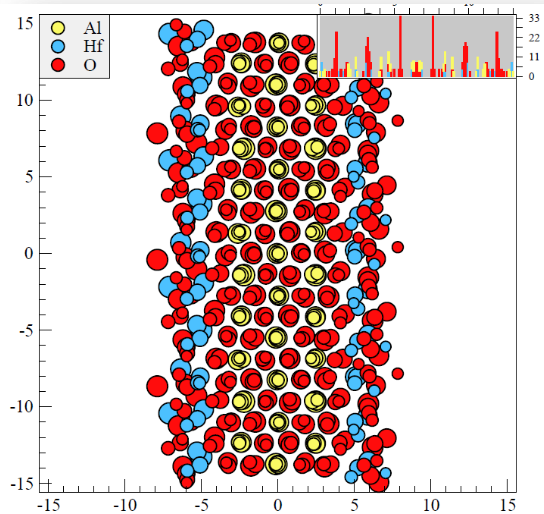


This is a *general* grain boundary!

3D Model + HAADF-STEM Simulations



DFT Simulations

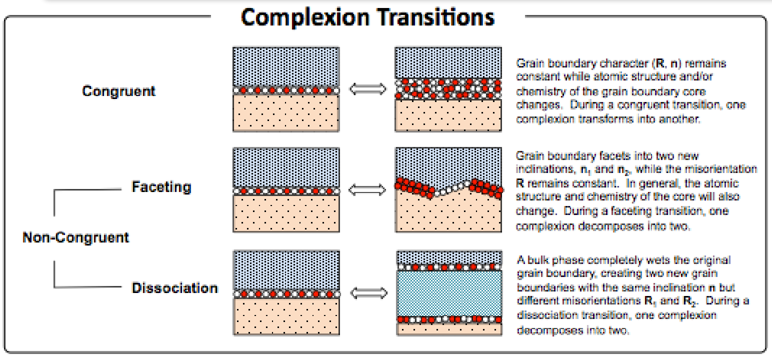


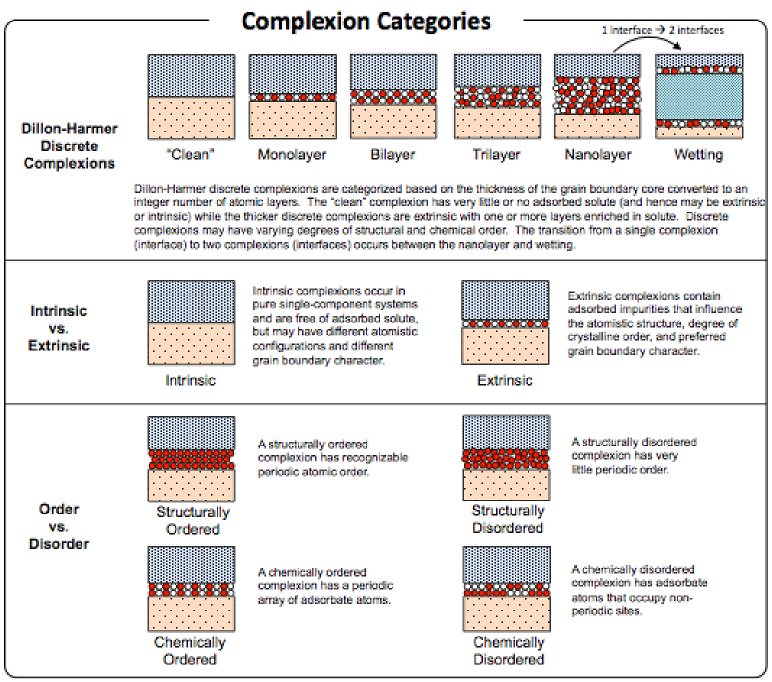
Acta Mat Overview: Grain Boundary Complexions

Acta Materialia Overview *Submitted May 3, 2013*

"Grain Boundary Complexions"

Patrick R. Cantwell, Ming Tang, Shen J. Dillon, Jian Luo, Gregory S. Rohrer, Martin P. Harmer

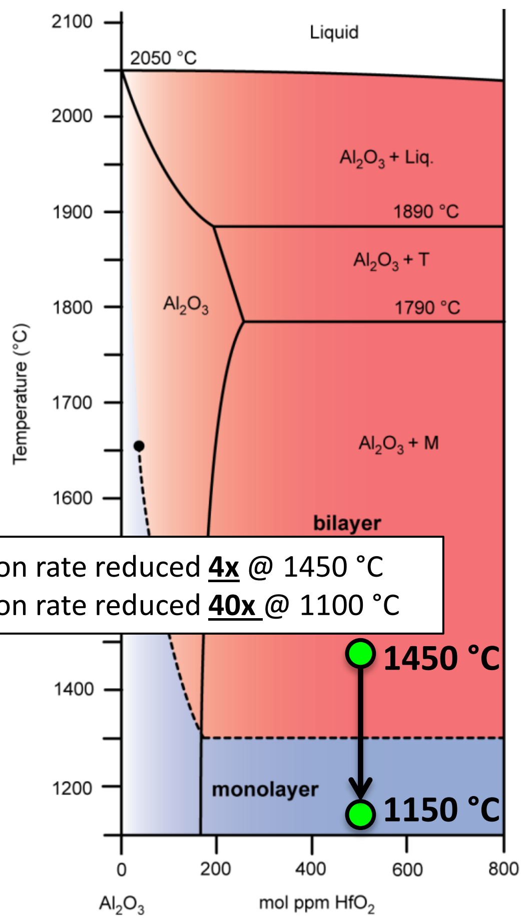




Complexion Transitions	*Defined by Geometry (grain boundary character)*	Congruent Transition	Complexion transitions that occur without a change in grain boundary character (**R** and **n** remain invariant); usually involves changes in atomic structure and composition of the grain boundary core
		Non-congruent Transition	Complexion transitions that result in a change in grain boundary character (**R** or **n** (or both) change)
		Structural Transition	A complexion transition that occurs when a bulk thermodynamic parameter is varied (T, P, μ, etc) while all five interfacial thermodynamic parameters (**n**, **R**) are held constant [8]
		Faceting Transition	A complexion transition in which a single complexion decomposes into two complexions: During a faceting transition, the grain boundary plane normal **n** decomposes into $\mathbf{n}_1$ and $\mathbf{n}_2$ whose sum is equivalent to **n**
		Dissociation Transition	A complexion transition in which a single complexion decomposes into two complexions: During a dissociation transition, a single grain boundary dissociates into two new interfaces, separated by a new phase, with misorientation $\mathbf{R}_1$ and $\mathbf{R}_2$ whose net misorientation is equal to the original misorientation **R**, i.e. $\mathbf{R} = \mathbf{R}_1 \times \mathbf{R}_2$. Also known as "wetting transition."
	Defined by Structure and/or Composition	Premelting Transition	The formation of a disordered, liquid-like film on a crystalline surface (or at a grain boundary, phase boundary, or free surface) at a temperature below the bulk melting temperature or solidus of the underlying crystal
		Prewetting Transition	Occurs when a nanolayer complexion of fixed equilibrium thickness forms at the interface in the thermodynamic vicinity of a wetting transition, i.e., near the temperature or composition at which a wetting transition would occur
		Adsorption Transition	A dramatic change (usually a first-order transition) in the composition of a grain boundary that occurs in the fractional coverage of solute at the grain boundary.
Complexion Categories	*Defined by Composition*	Intrinsic	Any grain boundary complexion that exists in pure systems such as an elemental metal.
		Extrinsic	Any grain boundary complexion that exists in a non-pure system, e.g. in a system that is intentionally doped with additional elements or a system that contains unintentional impurities
	Defined by Thickness and Composition	Dry	A grain boundary complexion with no adsorbed solute or submonolayer adsorption
		Moist	A grain boundary complexion with multilayer adsorption (bilayer, trilayer, nanolayer, etc).
		Wet	Refers to the existence of a bulk wetting film (solid or liquid) at a grain boundary
	Defined by Thickness and Composition	'Clean'	A grain boundary complexion with no adsorbed solute or submonolayer adsorption
		Monolayer	A grain boundary complexion in which the grain boundary core and adsorbed solute occupies a thickness equal to a single atomic layer
		Bilayer	A grain boundary complexion in which the grain boundary core and adsorbed solute occupies a thickness equal to a two atomic layers
		Trilayer	A grain boundary complexion in which the grain boundary core and adsorbed solute occupies a thickness equal to three atomic layers
		Nanolayer	A grain boundary complexion in which the adsorbed solute occupies a thickness greater than three atomic layers, but which is still finite, fixed, and governed by equilibrium thermodynamics. Equivalent to IGF.
		Wetting	Refers to the existence of a bulk wetting film (solid or liquid) at a grain boundary. There are two complexions (one on each side of the wetting film).
	Defined by Degree of periodicity	Ordered	A complexion which has a recognizable degree of structural or chemical long-range periodicity
		Disordered	A complexion with no recognizable long-range periodicity in either structure or composition
Related Terminology		Segregation	An equilibrium phenomenon that occurs in multicomponent materials, causing the composition of grain boundaries to differ from the overall composition at equilibrium
		Adsorption	Used interchangeably with 'segregation' when speaking of grain boundaries, the term 'adsorption' was originally used to discuss the analogous phenomenon when it occurs at surfaces
		Intergranular Film (IGF)	Films that are approximately 1-2 nm that have been widely observed at grain boundaries in various ceramics that contain impurities such as Si_3N_4 with SiO_2 impurities, ZnO with Bi_2O_3 impurities, and $SrTiO_3$ with TiO_2 impurities. IGFs are referred to as "nanolayers" under the Dillon-Harmer categorization scheme.

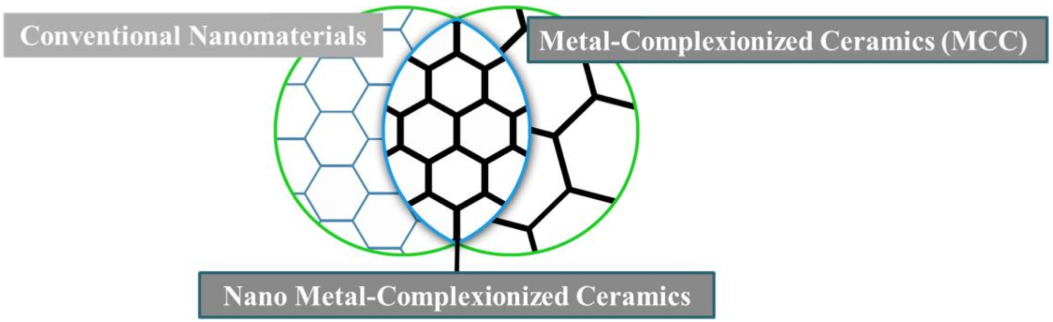
Potential Breakthroughs

Understanding Oxidation in Al_2O_3-HfO_2



Oxidation rate reduced **4x** @ 1450 °C
Oxidation rate reduced **40x** @ 1100 °C

Metal-Complexionized Ceramics



Understanding the Mechanism of Nanocrystalline Thermal Stability

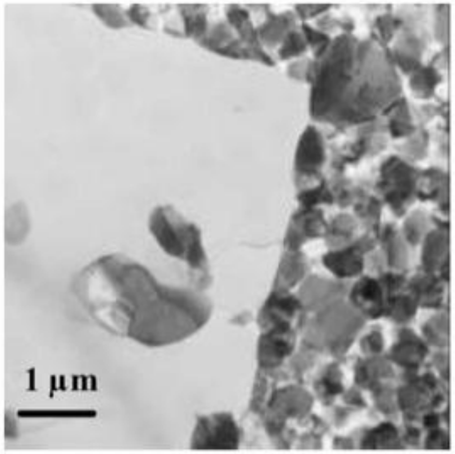


Fig. 3. Bright field TEM micrograph showing the embedded grains in the late stage abnormal grain growth microstructure.
G.D. Hibbard et al., Scripta Mat. 47 (2002) 83-87

Scientific Barriers & Grand Challenge

Internal Interfaces are Difficult to Study!

Surface Science & Surface "Phase" Transitions
- A relatively mature field…

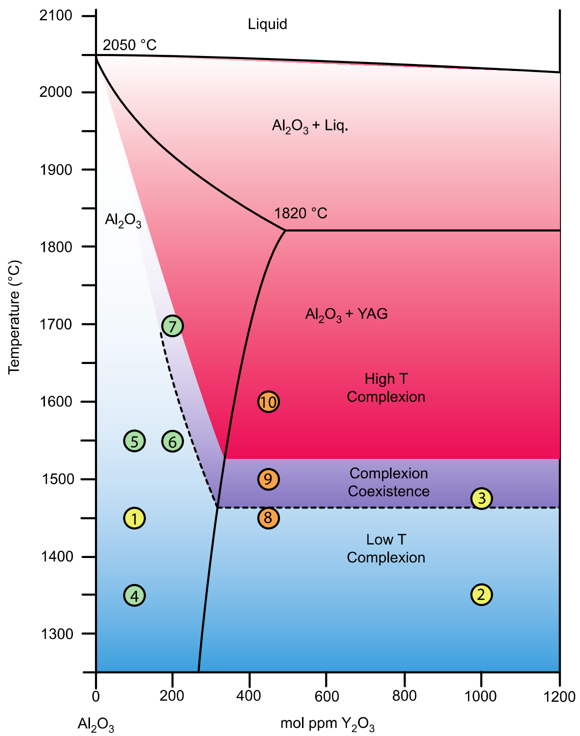
The Phase-Like Behavior of Grain Boundaries
- Discussed since at least 1968 (EW Hart)
- Experimental study difficult, even with aberration-corrected STEM

Grand Challenge:

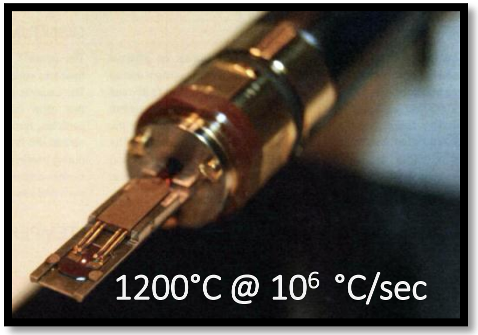
Grain Boundary Complexion Diagrams
- Analogous to bulk phase diagrams
- Bulk phase diagrams have been developed intensively over decades
- Grain boundaries have 5 more thermodynamic degrees of freedom!

Sub-Challenge: Studying Complexions at Equilibrium
- Does rapid quenching reveal the high-T complexions?
- Need in-situ TEM hot stage experiments
- Need other experimental techniques, too

Al_2O_3-Y_2O_3 Complexion Diagram



In-Situ TEM Hot Stage



Backup slides...

Future Work

1) **In-situ Hot Stage STEM**
   - Nanocrystalline thermal stability (and instability initiation at GBs)
   - Direct observation of complexion transitions

2) **TTT Diagrams**
   - How do complexions nucleate and grow?
   - “Sandwich” experiments

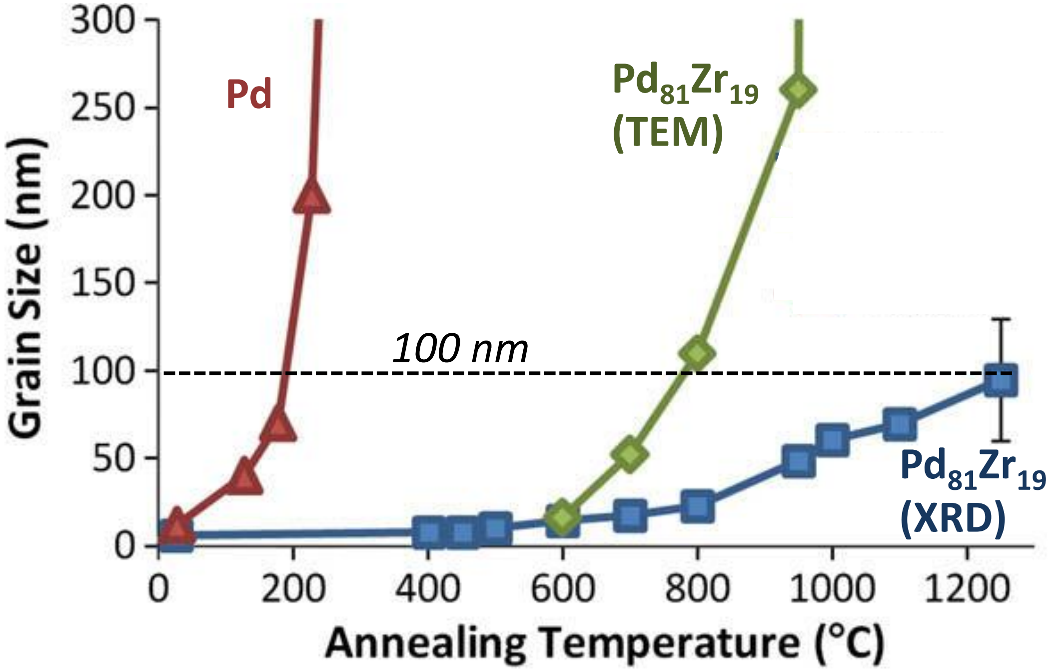
3) **Complexion Diagrams**
   - HfO_2-doped Al_2O_3
   - Oxidation kinetics

4) **Nanocrystalline thermal stability: Ni-W, Cu-Zr, W-Ti**
   - Sputtered and electroplated
   - We observe multiple bulk phases in electroplated samples…

5) **Metal-Compexionized Ceramics (MCCs)**
   - At grain boundaries in Al2O3
   - Dopants under exploration: Cu, Ni, Cu-Ti, Ni-Al, Cu-Nb

6) **Electrically-conductive Al2O3 by Complexion Engineering**
   - ITO-doped Al_2O_3

Nanocrystalline Thermal Stability



B. K. VanLeeuwen, K. A. Darling, C. C. Koch, R. O. Scattergood, B. G. Butler, Thermal stability of nanocrystalline Pd81Zr19. Acta Mater. 58, 4292 (2010).

GB mobility

GB energy

GB curvature

GB velocity

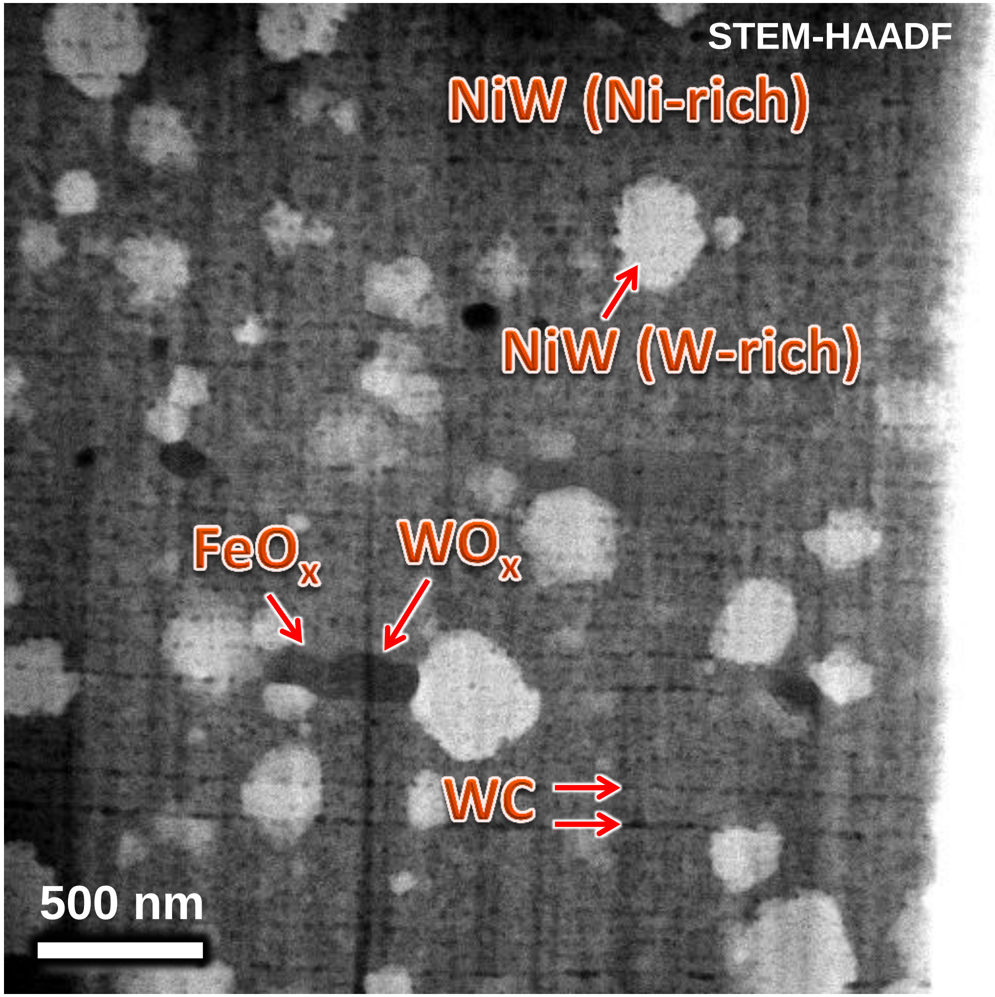
$$v = M \underbrace{g \kappa}_{\text{Driving force for grain growth}}$$

Which explains thermal stability and instability?

Thermodynamics: g

Kinetics: M

Nanocrystalline Thermal Stability



<u>Ni-W Specimen Info</u>

- Electroplated Ni-W
- Nominally 20 wt. % W
- Annealed 700C 4 hours Ar-H_2

<u>Initial STEM-HAADF and EDS indicates 5 phases:</u>

- Ni-W (Ni-rich) normal grains of ~30 nm dia.
- Abnormal grains of…
  - Ni-W (W-rich)
  - WO_x
  - FeO_x
- Nanoparticles of WC (~10 nm dia.) in periodic rows

Isothermal TTT diagram for complexion transitions in Y-doped Al_2O_3